Title: ADSORPTION PROPERTIES AND STRUCTURE OF ADSORBENTS 2. AD-
SORPTION FROM SOLUTIONS BY ACTIVATED CARBON IN A WIDE RANGE
OF CONCENTRATIONS   (USSR)   (O. M. Dzhigit, A. V. Kiselev,
M. G. Terekhova, and K. D. Shcherbakova)

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ADSORPTION PROPERTIES AND STRUCTURE OF ADSORBENTS

2. ADSORPTION FROM SOLUTIONS BY ACTIVATED CARBON IN A WIDE RANGE

OF CONCENTRATIONS

O. M. Dzhigit, A. V. Kiselev, M. G. Terekhova, and

K. D. Shcherbakova

I.   Introduction

In the previous works of this series [1, 2] the influence of
the character of the porosity of activated carbons on the adsorption
of surface-activated substances from aqueous solutions was studied;
this influence led to a sharp drop in the number of adsorbed mole-
cules, with an increase of the length of the hydrocarbon radical, and
to an approximate constancy of the maximum volume adsorbed. The re-
sults of the investigation of the isotherms of adsorption from solu-
tions were compared further [3, 4] with the results of the investi-
gation of the isotherms of adsorption of vapors, and also of the
heats of adsorption and moistening. It was found that the volume of
liquid methyl alcohol adsorbed from vapors before the beginning of
capillary condensation is close to the maximum adsorbed volumes of
aliphatic alcohols and acids from aqueous solutions. These observ-
ations led to the conclusion concerning the solid filling of the
micro-pores of the carbons studied by molecules of substances adsorbed
from vapors and solutions. Furthermore [5] , adsorption from solu-
tions by a series of carbons with a varying degree of activation was
investigated; and it was found that in proportion to the expansion
of the pores there occurs a gradual transition from the effect of
ultra-porosity to a constancy of the maximum adsorbed volume, and
further, to phenomena characteristic of large-pored and non-porous
adsorbents.

Solutions of substances of limited solubility in water were
chiefly used in these investigations. In the cases of adsorption
of butyric and acetic acids, which are mixable with water, it was

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found that the adsorption passes through a maximum, after which it begins to deep slowly with the further increase of concentration, approximately following a linear law. The maximum on the isotherms of adsorption at high concentration has been repeatedly noted in the literature [6 - 14]; and it fallows from the definition of adsorption as the excess of adsorbed substance in the adsorption volume in comparison with its content in an equal volume of free solution in equilibrium [13]. Kiselev and Shcherbakova [2] applied the equation connecting the determined adsorption x with the full content of adsorbed substance a in the adsorption volume V_a at a concentration c:

$$x = a - V_a \cdot c,$$ (1)

With the solid filling of the adsorption space of the carbon (the volume of its micro-pores) V_a, magnitude a reaches a constant maximum value, and x begins to drop linearly with further increase of c: also in this zone

$$V_a = -\frac{\partial x}{\partial c},$$ (2)

if V_a does not depend on c.

Such a characteristic of isotherms of adsorption passing through a maximum and dropping with the further increase of concentration was also found by the calculation of adsorption from the dependence of the surface tension of aqueous solutions of alcohol on the concentration (Guggenheim and Adam [13]) for the boundary between an aqueous solution and air; and also from the dependence of the adhesional tension on the concentration for the boundary between a solid body and a solution (Bartell and Benner [14]). The latter authors used formulae similar to (1), and found the approximate constancy of a in a wide range of concentrations. Treatment with the aid of Formula (1) of the isotherms calculated by Guggenheim and Adam for the plane between an aqueous solution of alcohol and air lead to the same conclusion.

Thus, the recorded characteristics of the isotherms of adsorption

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of surface-active substances mixible with a solvent (the adsorption passes through a maximum and then drops approximately lineally) are equally typical for the case of adsorption by solid bodies and for adsorption on liquid surfaces.*

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* A similar case takes place with the adsorption of gases, but at rather high pressures.

Semenchenko in 1932 gave a theory of such an isotherm for the case of adsorption from solutions on liquid surfaces /15, 16/, which was verified in his laboratory by measurements of the surface tension of amalgams and fusions /17, 18/. Starting from the principle of Boltzmann and assuming a solid filling of the volume of the solution and the surface layer with the components of the solution, Semenchenko obtained a formula for the isotherm of adsorption containing a term lineally decreasing with the concentration.

For the concentration of an adsorbed substance in a given element of adsorption volume c^ω Semenchenko obtained the expression

$$c^\omega = \frac{bc^\alpha}{1 + V_m(b-1)c^\alpha} \qquad (3)$$

where c^α is the concentration in a solution in equilibrium, and V_m is the molar volume; and the magnitude b is connected with change of potential energy $\mathcal{U}$:

$$b = e^{-\frac{\mathcal{U}^\omega - \mathcal{U}^\alpha - (\mathcal{U}_o^\omega - \mathcal{U}_o^\alpha)}{kT}} \qquad (4)$$

(index 0 refers to the solvent)*. Furthermore, Semenchenko estimated the change of potential energy with the aid of a representation of the generalized moment.

We may obtain a similar formula for adsorption on a solid body. Let us examine the adsorption on adsorbent 1 from a solution of a surface-active substance 3 in a solvent 2. From the conditions of

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* This same formula may also be obtained thermodynamically from the equation of the chemical potentials of the components of the solution in the surface layer and in the volume: $\mu^\omega = \mu^\alpha$, where $\mu = \mu^o(T) + RT \ln f c =$ $\mu^o(T) + \mathcal{U} + RT \ln c$, where $\mu^o(T)$ does not depend on the situation of the molecule; and f is the absolute coefficient of activity, which may be expressed by the potential $\mathcal{U}$ of an external (for example, gravitational, electrostatic, etc.) and molecular field, acting in the element of volume in question with the concentration c.

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We may obtain a similar formula for adsorption on a solid body. Let us examine the adsorption on adsorbent 1 from a solution of a surface-active substance 3 in a solvent 2. From the conditions of equilibrium of substances 2 and 3 in the element of volume of the surface layer ω and in the free volume of the solution a and from the conditions of displacement (Semenchenko [16], Guggenheim and Adam [13]):

$$c_3^\omega \omega + \dots \omega_v \omega \quad 1; \quad c^a V_v a, \quad a_v a \qquad (5)$$

we obtain:

$$c_3^\omega = \frac{\dots}{1 + \dots (V \dots a)} a \qquad (6)$$

Here

$$b = \frac{\omega}{\omega} \cdot 1 \qquad (7)$$

where

$$b = \dots - 4_3^\omega - 4_2^a - (4_2^\omega - 4_2^a) \qquad (8)$$

For obtaining the adsorption x we must calculate the integral in the expression:

$$x = \int_{}^{V_a} c^a v \dots a \dots \qquad (9)$$

In general the calculation of the integral requires a knowledge of the distribution of c^ω according to the volume V; furthermore, the boundary of the adsorption volume may also depend on the concentration. In certain particular cases, however, the problem is simplified. In the case of adsorption on a smooth surface $\underline{s}$, the adsorption volume is proportional to the thickness of the surface layer δ ($V \dots \delta$), which is constant during monomolecular adsorption of symmetrical molecules, so that c_3^ω does not depend on it. We may also consider V and c^ω constant in the case of adsorption in fine pores during their solid filling with surface-activated material, that is, in the zone of linear fall of the isotherm beyond the maximum.

In these cases

$$x_3 \cong (c_3^\omega - c_3^a) V_a \qquad (10)$$

and we obtain the following approximate equation for the isotherm of adsorption on a solid body:

$$x_3 \cong \frac{V_a b' c_3^a}{1 + (b' V_3^\omega - V_a^a) c_3^a} - V_a c_3^a \qquad (11)$$

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Inasmuch as magnitudes $V_3 \omega$ and $V_2 \alpha$ cannot differ greatly from one another,

$$b' V_3 \omega - V_2 \alpha = V_3 \qquad (12)$$

where V_3 is the molar volume of the pure component 3 in a liquid condition. Further

$$b' = b_0 e^{q/RT} \qquad (13)$$

where q is the average molar heat of adsorption from the solution. For strongly adsorbed substances, b' constitutes, probably, a magnitude of the order of $10^{?}$, so that in comparison with it one may disregard the unit, and (11) assumes a simpler form:

$$x_3 = \frac{V_a b' V_3 \omega c_3 \alpha}{1 + V_3 \omega b' c_3 \alpha} \qquad (14)$$

This formula is quite similar to the one used by Semenchenko for the case of adsorption n the surface of a liquid, containing in the index of magnitude b' the difference of the generalized moments of the components of the solution. Formulae (14) and (13) are correct for any form of interaction between molecules of components of the system. In general b' depends on the concentration.

Comparing (14) and (1), we see that the full content of the adsorbed substance in the adsorption volume V_a is expressed by the formula

$$x_3 = \frac{V_a b' c_3 \alpha}{1 + V_3 \omega b' c_3 \alpha} \qquad (15)$$

With the increase of $c \alpha$ this magnitude tends toward a definite limit

$$x_3 = \left(\frac{V_a}{V_3 \omega} \right) \qquad (16)$$

Let us now turn our attention to the fact that the product of $b' V_3 \omega$ stands in the denominator of the first term of (14) and (15). It is evident that the larger it is, the sooner it will be possible with the increase of concentration $c_3 \omega$ to disregard the unit in the denominator, and then the isotherm of adsorption will be subject to the simple equation

$$x_3 = \frac{V_a \omega}{V_3} - V_a c_3 \alpha. \qquad (17)$$

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This equation must be almost linear, because when the limiting value $\underline{a}$ is reached the magnitude $v_3{}^w$ cannot change at all essentially.

For the magnitude of the concentration, corresponding to the maximum of adsorption, Semenchenko gave the formula

$$(c_3^a)_{x = x_{max}} = \frac{\sqrt{b} - 1}{v_3 b}, \qquad (18)$$

from which it follows for strongly adsorbed substances that

$$(c_3^a)_{x = x_{max}} \approx \frac{1}{v_3 \sqrt{b}},$$

that is, with the increase of molar heat of adsorption and of molar volume of the surface-active component, the maximum on the isotherm of adsorption is displaced toward the smaller concentrations in equilibrium. This conclusion may be easily verified experimentally.

The formulae obtained may find other important application. It follows from (17) that in the zone of linear drop of adsorption with the increase of concentration Equation (2) is correct; that is, it is possible to determine the magnitude of the adsorption space V_s. The second constant of Equation (17) permits one to determine $v_3{}^w$, that is, to make a few conclusions about the condition of the substance adsorbed from solutions.

In the case of substances of limited solubility, the term $V_a c_3^a$ in (14) becomes small. In the case of substances of slight solubility, it is generally possible to disregard it, since magnitude x_3 practically coincides with a, (1), and therefore tends toward the limit. Formulae (18) and (17) show that in this case we may estimate the magnitude of the adsorption volume according to the formula:

$$V_a \approx \omega_\infty \, v_3{}^w \approx x_\infty \, v_3, \qquad (20)$$

which was used by us in previous works [1, 2].

Extensive experimental material has been obtained in our laboratory, which qualitatively confirms the conclusions made. In this work we will limit ourselves to a presentation of the results of the investigation of the isotherms of adsorption by carbon representatives of a homologous series of aliphatic acids and alcohols from aqueous solutions. Here we have cases when $\overline{Q}$ is much larger than $\overline{RT}$, and both

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$\overline{Q}$ and v_3 increase in the homologous series. According to Semenchenko /Formula (19)/ we must expect a noticeable displacement toward smaller concentrations of the maximum on the isotherms of adsorption with the increase of the number of atoms of carbon in the adsorbed molecules.

II. Experiments

On the basis of the considerations expounded in the present work, we made an attempt to investigate in greater detail the adsorption from solutions by activated carbon not only of substances of limited solubility in water, but also of substances mixible with water in all proportions. For this we used a more highly activated carbon from dried apricot pits, rinsed in hydrochloric acid and water to an ash content of 0.66 percent.*

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* Carbon No. 4 in the series studied previously /5/.

Experiments with evacuated carbon and a solution of acetic acid showed that the presence of air exerts practically no influence on the magnitude of adsorption (Fig. 5). Therefore, in the remaining cases the carbon was dried in a vacuum in large portions, after which it was in communication with dry air, and in such a form it was used for the adsorption experiments.

The investigation of the isotherms of adsorption was conducted for all members of a homologous series of normal aliphatic alcohols and acids, beginning with methyl alcohol and formic acid and ending with heptyl alcohol (only slightly soluble in water) and substances containing ramified chains and cycles. For substances mixible with water the adsorption was measured in a wide zone of concentrations up to highly concentrated solutions; and in the case of substances of limited solubility the measurements were made up to concentrations constituting 80-90 percent of that of saturated solutions. The concentrations were measured, as previously, with the aid of a Zeiss interferometer. The calculation of adsorption was conducted according to the usual formula:

$$x_3 = \frac{v_0}{m_1}(c_3^o - c_3^a) = \frac{1}{m_1}(\eta_3^o - v_0 c_3^a), \qquad (21)$$

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where V_o is the volume of the poured solution with a volumetric con-

centration of c_j^o ; and m_j is the weighed portion of the adsorbent.

In some experiments we measured individually the full quantity of

substance 3, n_j^o introduced into an ampoule. It was noted by Kiselev

and Shcherbakova [2] that a strict expression for the determination

of x_j corresponding to the $\Gamma_j^{(v)}$ of Guggenheim and Adam [13] is the

formula:

$$x_j = \frac{V_o}{m_j}\left(c_j^o - c_j^\alpha\right) - \frac{\Delta v}{m_j} \cdot c_j^\alpha \quad (22)$$

where Δv is the change in volume of the solution, produced by adsorp-

tion. With small c_j^α the magnitude of the correction term may be dis-

regarded. Apparently, it is small in the entire interval of concen-

trations investigated by us.*

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* The measurements of the heats of adsorption of vapors show [3, 4]
that a strong compression may be expected only in a volume of the
order of 10 percent of V_a. When $V_a \cong 0.5$ cm^3/g, and the change
of volume is up to 20 percent, $\Delta v \cong 0.1 \cdot 0.2 \cdot 0.5 = 0.01$ cm^3/g,
which at the greatest value of $c_j^\alpha \cong 10$ μM leads to the magnitude
of the correction term at 0.1 μM/g, which is still lower than 10
percent of x_j at this value c_j. The general expression for the
relative magnitude of the correction term will be given in the
following work; it has the form

$$\frac{\Delta v}{V_o} \cdot \frac{a_j^\alpha c_j}{1 - c_j/c_j^o}$$

The approximate formula (21) is convenient for treatment of the

measurements, since magnitude $\frac{V_o}{m_j}\left(c_j' - c_j^\alpha\right)$ does not depend on the ratio

$\frac{V_o}{m_j}$; for in the precise formula (22) the magnitude x_j and $\frac{\Delta v}{m_j} c_j^\alpha$ do

not depend on it. The magnitude x (or $\Gamma_j^{(v)}$) possesses the advantage

in that it leads directly to the full content a in the adsorption

volume, which is of interest for the theory.

III. Results and Discussion

1) Adsorption of Normal Aliphatic Acids and Alcohols of Limited

Solubility

In the zone of small concentrations the adsorption of acids and

alcohols increases with the increase of the number of carbon atoms

per molecule, in accordance with the "straight series of Traube"

(Figs. 1 and 2). In the case of substances of limited solubility in

water, the adsorption tends toward the limit with further increase

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of concentration (Figs. 3 and 4).* The data given in Table 1 show

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* At the present time we have worked out a method for measuring
adsorption from a solution up to the concentration corresponding
to saturation. In Fig. 4 the results obtained for heptyl alcohol
are given. The dotted line corresponds to the extrapolation of
the curve corresponds to the effect of capillary stratification
found by us, which is described in a separate report /19/.

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that the magnitudes of the maximum adsorbed quantities (mN/g) de-

crease with the increase of the number of carbon atoms per molecule

(consequently corresponding to the "inverse series of Traube"), at

the same time that the maximally adsorbed volumes (cm^3/g) calculated

according to (20) are close to constancy /5/.

Thus, for this carbon the rule found by us previously is ful-

filled: the rule of the approximate constancy of the maximum ad-

sorbed volume of normal acids and alcohols strongly adsorbed from

aqueous solutions.

The magnitude of this volume is about 0.54 cm^3/g, and represents

fundamentally the volume of the micro-pores of this carbon. The

isotherm of sorption of vapors of methyl alcohol by this carbon has

the usual form for such a type of carbon /3, 4, 20/. At the point

of the beginning of sorption hysteresis the volume of liquid methyl

alcohol adsorbed from vapors amounts to 0.53 cm^3/g; this magnitude,

like that for other carbons of this type studied previously, /3, 4/,

is close to the volume of the micro-pores.

2) Adsorption of Aliphatic Acids and Alcohols of Unlimited Solu-

bility in Water

Isotherms passing through the maximum were obtained in all

cases of adsorption of low-molecular members (of unlimited solubility

in water) of these same homologous series (Figs. 5 and 6). An almost

linear decrease of adsorption x with the increase in concentration

was found by us in the zone of large concentrations for all sub-

stances containing more than one carbon atom per molecule, within the

limits of accuracy of the determinations of magnitude x, according to

(21), especially for propyl alcohol and butyric acid. As may be seen

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from the diagrams, the maximum of adsorption is displaced to the zone of smaller concentrations with the increase of the hydrocarbon radical, in accordance with the requirement of the theory (19) (the increase of $_{ij}$ and Q). The approximate values of the concentrations corresponding to the maxima are given in Table 2.

The results obtained confirm qualitatively the theoretical representations given in the introduction concerning the general form of the isotherm of adsorption of surface-activated substances in a wide zone of concentrations.*

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* A comparison with the results of direct measurements of heats of adsorption which are being conducted in our laboratory will be made separately.

The absolute magnitudes of the inclinations of the lineally falling branches of these isotherms are given in Table 3. From this table it is evident that they increase with the increase of the number of carbon atoms in the adsorbed molecules, approaching the volume filled by higher-molecular substances of limited solubility (Table 1); and for propyl alcohols and butyric acid they become practically equal to it.

The smaller magnitudes-- $\frac{\partial x}{\partial}$ for lower acids and alcohols are apparently due to the fact that at the concentrations studied the molecules of these substances do not completely fill the entire volume of the micro-pores of this relatively large-pored $\underline{/5/}$ carbon, so that for them $V_a < v_{micro}$, at least in the zone that has been studied. The volume of micro-pores remaining free is occupied in these cases by a solution in equilibrium even with large concentrations; this is true because the tendency toward displacement of water weakens due to the large quantity of polar groups of--COOH or --CH entering the micro-pores in the case of adsorption of short molecules of acids and alcohols possessing a smaller energy of adsorption.

These results are represented graphically in Fig. 7. In the upper part the dependence of the maximal adsorption $\underline{x}$ on the number

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of carbon atoms in the adsorbed molecules is shown; in the lower part,
the same for the magnitudes of the volumes: $\frac{9}{9}$ (for the lower
members of the series) and (for the members of the series
of limited solubility).

It is also possible to calculate the magnitudes ν_i^{ω} from the
linear branch of the isotherms (Table 4).

The table shows that these magnitudes are close to the values of
the molar volumes of aliphatic acids and alcohols in the liquid state
under ordinary conditions. It is impossible to make any further con-
clusions from this comparison, for the calculation of the correction
term in Formula (22) would be required for this. In this respect
independent determinations of the density of the substance in the
adsorption volume would have a very important significance.

We have previously pointed out [1-5] that normal activated car-
bons used for sorption of vapors possess three groups of pores: very
fine micro-pores, fundamentally corresponding to the adsorption space
of the carbon; larger pores, filled by capillary condensation in the
process of adsorption of vapors of methyl alcohol; and finally, very
large apertures and cavities, which are filled during moistening, and
which do not play a vital role for the sorption of vapors even at very
high relative pressures. The last group of pores is not of interest
in the investigations of adsorption equilibria.

There apparently exists a rather sharp boundary between the
first and second groups of pores in activated carbons of the type in
question, which is indicated by the following facts: 1) the sorption
hysteresis found by us previously [3, 4] and noted recently [20] with
a sharp drop of the desorption branch at its beginning, where the
isotherm of adsorption rises very weakly; 2) the sharp decrease in
differential heat of adsorption during transition to the zone of
capillary condensation in the larger pores [3, 4, 21]; 3) the
significantly smaller magnitude of the surface of the film on which
capillary condensation begins [22], in comparison with the possible

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surface of the carbon, which indicates the filling of the micro-pores before the beginning of capillary condensation.

Therefore, we observe for such carbons an approximate constancy of the maximum adsorbed volume of strongly adsorbed normal acids and alcohols; and the nearness of this volume to the volume of methyl alcohol adsorbed from vapors at the point of beginning of hysteresis, where a rather abrupt transition to capillary condensation takes place. Smaller volumes are filled in the case of lower members of the series of normal acids and alcohols, due to the smaller energies of adsorption in relation to the carbon in the process of adsorption from solutions. At very high concentrations we may expect in these cases an increase of % up to the volumes filled in the process of sorption of vapors at high relative pressures of vapor, that is, in the zone of capillary condensation.*

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* In connection with this, the investigation of adsorption from solutions of substances of limited solubility close to saturation is of great interest; here it is possible for the large pores to be filled as a result of the capillary stratification of solutions, in a manner similar to that of the capillary condensation of vapors /19/.

In the case of butyric acid the continuation of the linear portion of the isotherm intersects the axis of the abscissao near the concentration corresponding to the pure adsorbed substance ($c_j^a = \frac{1}{V_m}$). It is quite probable that the fall of the isotherms in this zone is delayed, and the isotherms approach zero asymptotically when $c_j^a = \frac{1}{V_m}$. This would correspond to a certain increase of magnitudes $\underline{a}$, that is, to the filling of larger pores, or a denser packing of the molecules of the adsorbed substance.

It is impossible to make any more detailed and definite conclusions in this direction; for experimental work in the zone of high concentrations involves great difficulties, and Formula (21) becomes inexact.

3) <u>Adsorption of Isomeric Substances and Substances of Cyclic Structure</u>

The results of the investigation of a number of other substances

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are given in Figure 8 and in Tables 5 and 6. The ramification of the hydrocarbon chain and the presence of a hydrocarbon ring decrease the degree of filling of the micro-pores. Moreover, as in the case of the birch charcoal previously studied /27, the flat molecules of phenol are capable of filling the volume of the micro-pores most densely; a smaller volume of maximum adsorption corresponds to the distorted and hydrogenated molecules of cyclohexanol.

IV. Conclusions

1. The general form of the isotherm of adsorption of surface-active substances from solutions in a weakly-adsorbed solvent was considered. It was shown that in the case of adsorption on a solid surface the isotherm equation developed by Semenchenko and used by him for adsorption on liquid surfaces is correct.

2. The isotherms of adsorption from aqueous solutions by carbon made from pits in a wide zone of concentrations were determined for all normal aliphatic acids from formic to caprylic; for all normal aliphatic alcohols from methyl to heptyl; also for two isomeric aliphatic alcohols and a cyclic alcohol and phenol.

3. The adsorption by this carbon of acids and alcohols of normal structure that are of limited solubility in water follows the rule of the constancy of maximum-adsorbed volumes.

4. The adsorption of acids and alcohols mixible with water passes through a maximum with the increase of concentration, and thence decreases approximately lineally.

5. The inclinations of these lineally falling branches of isotherms, which are connected with the magnitude of the adsorption volume, approach the volume of the micro-pores of the carbon investigated.

6. In accordance with the theory of Semenchenko, the position of the maximum on the isotherms of adsorption is displaced to the zone of smaller concentrations with the increase of the number of carbon atoms in the adsorbed molecules.

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7. The maximal adsorption (excess) of dissolved acids and alcohols passes through a maximum with the increase of the number of carbon atoms, at the same time that the full volume of the adsorbed substance in the micro-pores of the carbon attains its maximum value.

8. The ramification and cyclization of the adsorbed molecules lowers the degree of their filling of the micro-pores of the carbon studied.

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Translation of captions of diagrams:

Fig. 1 (p. 112): Isotherms of adsorption of normal aliphatic acids from aqueous solutions by carbon made from pits in the zone of small concentrations: 1 - formic; 2 - acetic; 3 - propionic; 4 - butyric; 5 - valeric; 6 - caproic; 7 - heptylic; and 8 - caprylic.

Fig. 2 (p. 112): Isotherms of adsorption of aliphatic alcohols from aqueous solutions by carbon made from pits in the zone of small concentrations: 1 - methyl; 2 - ethyl; 3 - normal propyl; 4 - isopropyl; 5 - normal butyl; 6 - normal amyl; 7 - normal hexyl; and 8 - normal heptyl.

Fig. 3 (p. 113): Isotherms of adsorption of normal aliphatic acids of limited solubility from aqueous solutions by carbon made from pits; 1 - valeric; 2 - caproic; 3 - heptylic; and 4 - caprylic. The vertical dotted line corresponds to a saturated solution.

Fig. 4 (p. 113): Isotherms of adsorption of normal aliphatic alcohols of limited solubility from aqueous solutions by carbon made from pits: 1 - butyl; 2 - amyl; 3 - hexyl; and 4 - heptyl. The vertical dotted line corresponds to a saturated solution.

Fig. 5 (p. 115): Isotherms of adsorption of lower aliphatic acids from aqueous solutions by charcoal made from pits: 1 - formic; 2 - acetic (a corresponds to the evacuated carbon and the solution); 3 - propionic; 4^b - butyric. Curve 4 corresponds to the isotherm of the fullcontent of butyric acid in adsorption volume $\underline{a}$. The vertical dotted line corresponds to the concentration of pure butyric acid.

Fig. 6 (p. 115): Isotherms of adsorption of lower aliphatic alcohols from solutions by carbon made from pits: 1 - methyl; 2 - ethyl; 3 - normal propyl; and 4 - isopropyl. The vertical dotted line corresponds to the concentration of pure normal propyl alcohol.

Fig. 7 (p. 116): Dependence of the maximal adsorption by carbon made from pits (mM/g, upper part) and the adsorbed volume (cm³/g, lower part) on the number of carbon atoms per molecule. Acids are on the left; alcohols, on the right. The light circles in the lower part of the diagram represent the results of calculation according to Equation (2) (substances mixed with water); the black circles, the results of calculation according to Equation (20).

Fig. 8 (p. 118): Isotherms of adsorption by carbon made from pits from aqueous solutions of alcohols of varying structure: 1 - isobutyl-carbinol; 2 - dimethylethyl-carbinol; 3 - phenol; and 4 - cyclohexanol.

Keys to Tables:

Table 1 (p. 114):

Magnitudes of Maximum Adsorption of Normal Aliphatic Acids and Alcohols of Limited Solubility from Aqueous Solutions by Carbon Made from Pits

Adsorbed substance	$x_\infty \left(\frac{mM}{g} \right)$	$x_\infty \cdot v \left(\frac{a)}{cm^3} \frac{}{g} \right)$	$a_\infty \left(\frac{mM}{g} \right)$	$a_\infty \cdot v \left(\frac{b)}{cm^3} \frac{}{g} \right)$
Acids:				
Valeric	4.7 [5]	0.52	4.9 [0]	0.53
Caproic	4.3 [5]	0.54	4.4 [5]	0.55
Heptylic	3.6 [5]	0.52	3.6 [5]	0.52
Caprylic	3.4 [5]	0.55	3.4 [5]	0.55
Average	—	—	—	0.54
Alcohols:				
Butyl	5.0 [5]	0.46	5.5 [0]	0.50
Amyl	4.8 [0]	0.52	5.0 [5]	0.53
Hexyl	4.4 [0]	0.55	4.4 [5]	0.55
Heptyl	4.0 [0]	0.57	4.0 [0]	0.57
Average	—	—	—	0.54

a)   is the millimolar volume of the pure adsorbed substance in the liquid state at 20° C.

b)   was calculated from x   according to (1), assuming   0.54, whichwhich followed from the data for slightly soluble substances, for which x   a .

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Table 2 (p. 114):

Value of Concentrations Corresponding to the Maximum on the Isotherms of Adsorption of Alcohols and Acids Mixible with Water

Adsorbed Acids	mM/L	Adsorbed alcohols	mM/L
Acetic	2 500	Ethyl	3 300
Propionic	2 000	Propyl	1 800
Butyric	1 800		

Table 3 (p. 116):

Magnitudes of $\frac{\partial}{\partial}$ in the Zone of Linear Fall of Isotherms of Adsorption for Aliphatic Acids and Alcohols Mixed with Water

Acids	$-\frac{\partial}{\partial}$ $\left(\frac{m}{s}\right)$	Alcohols	$\frac{\partial x}{\partial}$ $\left(\frac{1}{s}\right)$
Acetic	(0.8)	Ethyl	(0.4)
Propionic	0.46	Normal Propyl	0.53
Butyric	0.55	Isopropyl	0.53

Table 4 (p. 117):

Magnitudes of Molar Volumes of Acids and Alcohols, Calculated from the Linear Branches of Isotherms of Adsorption and from the Density of Normal Liquids at 20° C (cm/mole)

Acids	V_3^{ω}	V_n	Alcohols	V_3^{ω}	V_m
Acetic	54	57.1	Ethyl	69	58.4
Propionic	81	74.4	Normal propyl	85	75
Butyric	99	92			

Table 5 (p. 118):

Influence of Isomorization of Molecules of Alcohol with Five Carbon Atoms on Magnitudes of Maximum Adsorption (Substances of Limited Solubility in Water)

Adsorbed substance		$\frac{x_m}{\text{mM}}$ $\frac{}{q}$	$x_m \cdot V_m$ $\frac{cm^3}{q}$
Designation	Chemical formula		
Normal primary amyl alcohol	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	4.8 [0]	0.52
Isobutylcarbinol	$\frac{CH_3}{CH_3}CH-CH_2-CH_2OH$	4.2 [5]	0.46
Dimethyl-ethyl-carbinol	CH_3 CH_3-C-OH CH	3.6	0.39

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Table 6 (p. 119):

Influence of Cycles in a Molecule of Alcohol with Six Carbon Atoms
on the Magnitudes of Maximum Adsorption (Substances of Limited
Solubility in Water)

Adsorbed substance	X_∞ $\left(\frac{mM}{g}\right)$	$X_\infty \cdot V_m$ $\left(\frac{cm^3}{g}\right)$
Normal primary hexyl alcohol	4.4	0.55
Phenol	5.2 [5]	0.47
Cyclohexanol	3.6	0.38